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A novel Co(phen)$_2$/C catalyst for the oxygen electrode in rechargeable lithium air batteries

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A novel Co(phen)$_2$/C catalyst was prepared by coating cobalt(II) phenanthroline (phen) chelate on BP2000 carbon black and then heat treating in an inert atmosphere. The obtained Co(phen)$_2$/C product with 1.0 wt% cobalt loading exhibits similar morphology and porosity characteristics to those of the bare BP2000. X-ray diffraction measurements demonstrate a face-centered cubic (fcc) α-Co phase embedded in the carbon support after pyrolysis. Charge/discharge tests of the lithium-oxygen cells using the prepared Co(phen)$_2$/C catalyst show high discharge capacities of 4870 mAh g^{-1} (0.05 mA cm^{-2}), 3353 mAh g^{-1} (0.1 mA cm^{-2}) and 3220 mAh g^{-1} (0.15 mA cm^{-2}), respectively. The Co(phen)$_2$/C cathode exhibits reasonable reversibility with capacity retention of 1401 mAh g^{-1} (0.1 mA cm^{-2}) after 10 cycles. The superior electrochemical performance of the prepared Co(phen)$_2$/C catalyst and low cost of the phenanthroline chelating agent indicate that Co(phen)$_2$/C is a promising cheap catalyst for lithium-air batteries.

rechargeable lithium-air batteries, cobalt phenanthroline catalyst, oxygen electrode

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Recently, lithium-air batteries have attracted growing interest because they exhibit a huge theoretical specific energy of 11140 Wh kg^{-1} excluding O_2, which provides a practical energy density of an order of magnitude that is larger than the current high-performance lithium ion batteries. Besides, oxygen as an active material from the environment is essentially unlimited. The first lithium-air battery with a structure of Li|organic electrolyte|air was reported in 1996 by Abraham and Jiang [1], and further developed by many scientists over the world [2–15]. However, the investigation and development on lithium-air batteries is still in its initial stage. Much fundamental research is required before it can be considered for further technological applications. There are impressive challenges on the development of electrolyte systems and air cathodes [16–23].

As the specific capacity of rechargeable lithium air batteries is limited by the air cathode, the nature of the catalyst is important for fabricating higher capacity lithium air batteries [24–30]. Transition-metal macrocycles such as phthalocyanine, porphyrin, and their derivatives have emerged as some of the most promising non-noble oxygen reduction reaction catalysts (MN_x-based catalysts) [31–33]. Cobalt phthalocyanine as a catalyst for O_2 electrodes displays a considerable performance in lithium air batteries, which has been reported by Abraham's group [1]. However, cobalt phthalocyanine is too expensive for large scale application. It is very important to develop active catalysts with low cost for lithium air batteries. In this work we report an inexpensive non-noble catalyst Co(phen)$_2$/C prepared using a simple and cheap phenanthroline chelating ligand. Electrochemical performance of the prepared catalyst was investigated. Oxygen electrodes using the prepared Co(phen)$_2$/C catalyst could deliver high capacities for rechargeable lithium air batteries.

1 Experimental

The Co(phen)$_2$/C catalyst was prepared using BP2000 (American Cabot Co.) as a carbon support. The BP2000

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carbon was activated by refluxing with 30% H_2O_2 over night, washed with de-ionized water and then dried in a vacuum oven at 100°C for 4 h. The dried BP2000 powder was milled for 2 h in a planetary mill (Fritsch Pulversette-6) with an agate vessel.

Following is the preparation procedure for the $Co(phen)_2$/C catalyst. First, 0.046 g cobalt acetate was dissolved in 25 mL ethanol and 0.073 g phenanthroline ligand was added to form the $Co(phen)_2$ chelate. The obtained solution was mixed with 1.0 g activated BP2000 for 1 h under ultrasonic condition and then kept stirring for 2 h. After drying to remove ethanol, the resulting powder was heat treated at 900°C for 90 min under an argon atmosphere to obtain the final $Co(phen)_2$/C product with a 1.0 wt% Co loading.

The prepared $Co(phen)_2$/C catalyst and BP2000 were characterized using X-ray diffraction (D/max-2200/PC, Rigaku Co. Ltd., Tokyo) with filtered Cu Kα radiation. The XRD patterns were collected at room temperature by step scanning at the range of $20° \leqslant 2\theta \leqslant 80°$. The morphology of the samples was observed by transmission electron microscopy (TEM, JEM-2100). Porosity and BET surface areas for the samples were measured using a nitrogen sorption instrument (Micromeritics, ASAP2020). The surface situation of the oxygen electrodes after the first discharge and first charge was examined using a SIRION 200 scanning electron microscopy.

The oxygen electrodes were prepared by casting a mixture of $Co(phen)_2$/C catalyst and polytetrafluoroethylene (PTFE) binder in a weight ratio of 85∶15 onto carbon paper. The electrode disks with a diameter of 20 mm were punched and then dried at 120°C for 8 h. The mass load of the catalyst layer was 2 mg cm^{-2}. For comparison, oxygen electrodes using bare BP2000 as a catalyst were also prepared in the same way. The lithium-oxygen cells with Li metal as anode, oxygen electrode as cathode and polymer electrolyte membrane (PVDF-HFP-silica) as separator were assembled for electrochemical testing. The polymer electrolyte membrane was soaked in an electrolyte (consisting of 1 mol L^{-1} $LiPF_6$ dissolved in a mixture of propylene carbonate (PC) and diethyl carbonate (DEC), 1∶1 in volume) before assembly. All processes of assembling and dismantling the battery cells were carried out in an argon atmosphere in a glove box. The structural demonstration of the assembled lithium-oxygen battery is shown in Figure 1.

The lithium-oxygen battery cells were tested in a 1 atm (1 atm=1.03×10^5 Pa) oxygen atmosphere using a battery test system (LAND CT2001 A model, Wuhan Jinnuo Electronic Co., Ltd) at 25°C. Discharge/charge curves were recorded galvanostatically with various current densities at the voltage range of 2.0–4.5 V. The specific capacities are normalized with respect to the mass of catalyst (i.e. $Co(phen)_2$/C catalyst or bare BP2000 catalyst) in the cathode. Electrochemical impedance spectroscopy (EIS) of the lithium-oxygen cells was measured over a frequency range of $0.1–10^5$ Hz. All measurements were carried out under an oxygen atmosphere.

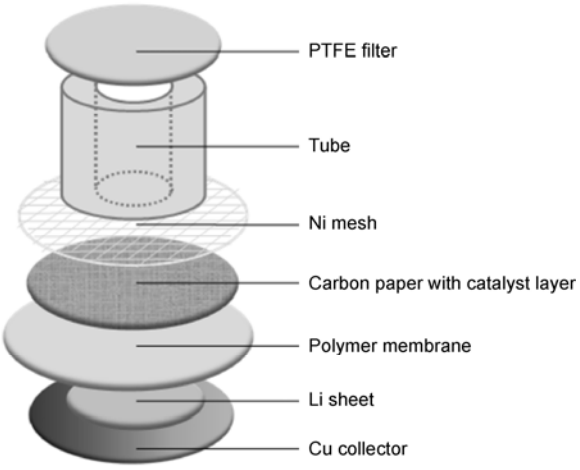

Figure 1 Schematic diagram of the lithium-air battery system.

2 Results and discussion

Powder XRD patterns of the prepared $Co(phen)_2$/C catalyst and the carbon support BP2000 are displayed in Figure 2. The XRD pattern of $Co(phen)_2$/C shows one prominent peak at around 44° and two weak peaks at 52° and 76°, corresponding to the Co(111), Co(200) and Co(220) planes, respectively, of a face-centered cubic (fcc) crystalline α-Co phase (PDF 89-4307). These results indicate that metallic cobalt was present on the carbon support surface after heat treatment.

Figure 3 shows the TEM images of BP2000 and the $Co(phen)_2$/C powder. It can be seen from Figure 3(a) that BP2000 presents high mesoporosity with both very small particle size and uniform size distribution. The morphology of $Co(phen)_2$/C in Figure 3(b) exhibits similar characteristic to that of the bare BP2000. This result indicates that the

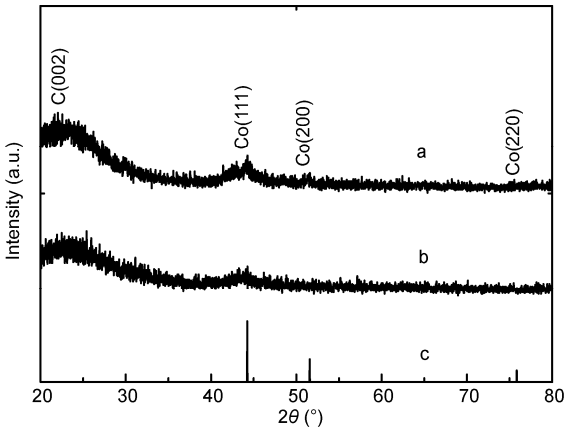

Figure 2 X-ray diffraction patterns of (a) $Co(phen)_2$/C, (b) BP2000, (c) PDF 89-4307.

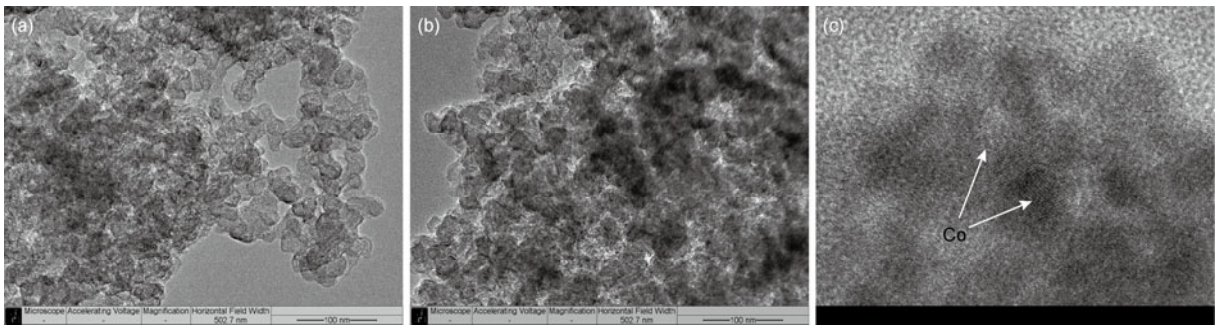

Figure 3 TEM images of BP2000 (a), Co(phen)$_2$/C (b) and (c).

cobalt loading did not obviously change the morphology characteristic of the carbon support. Figure 3(c) further reveals the presence of cobalt crystals on the surface of the carbon support in the Co(phen)$_2$/C catalyst.

The porosity of the Co(phen)$_2$/C catalyst and BP2000 has been investigated by nitrogen sorption analyses. Figure 4 shows the typical nitrogen adsorption-desorption isotherms for the samples. The isotherms of the Co(phen)$_2$/C catalyst and BP2000 show very similar characteristics with an adsorption hysteresis indicating the presence of mesopores. Moreover, both samples exhibit broad pore size distributions with pore sizes of less than 50 nm. The BET surface area of BP2000 is 1491 m^2 g^{-1} and the pore volume is 2.11 cm^3 g^{-1}. As the cobalt loading is only 1.0 wt%, the Co(phen)$_2$/C sample shows similar pore size distribution characteristics with that of BP2000. The Co(phen)$_2$/C sample shows a BET surface area of 1276 m^2 g^{-1} and a pore volume of 2.02 cm^3 g^{-1}. These results indicate that the Co(phen)$_2$/C catalyst almost remains almost the same surface structure characteristics of BP2000, and is consistent with the TEM observation.

Figure 5 shows the discharge and charge behavior of lithium-oxygen cells using Co(phen)$_2$/C and BP2000 oxygen electrodes at different current densities. The Co(phen)$_2$/C cathode shows a constant discharge potential plateau at about 2.82 V vs. Li/Li$^+$ under 0.05 mA cm^{-2} with a first discharge capacity of about 4870 mAh g^{-1}, which is 47% higher than that of the BP2000 cathode (3315 mAh g^{-1}, with a potential plateau at around 2.7 V vs. Li/Li$^+$). As the current density increased to 0.1 and 0.15 mA cm^{-2}, the discharge capacities of the Co(phen)$_2$/C cathode were 3353 and 3220 mAh g^{-1}, respectively. While the discharge capacities of the BP2000 cathode were only 2665 and 1898 mAh g^{-1}, respectively. In addition, the charge curves in Figure 5 obviously show that the Co(phen)$_2$/C cathode exhibits better charge behavior than that of the BP2000 cathode. The good performance of the Co(phen)$_2$/C cathode was attributed to the cobalt catalyst, which played a key role in promoting the

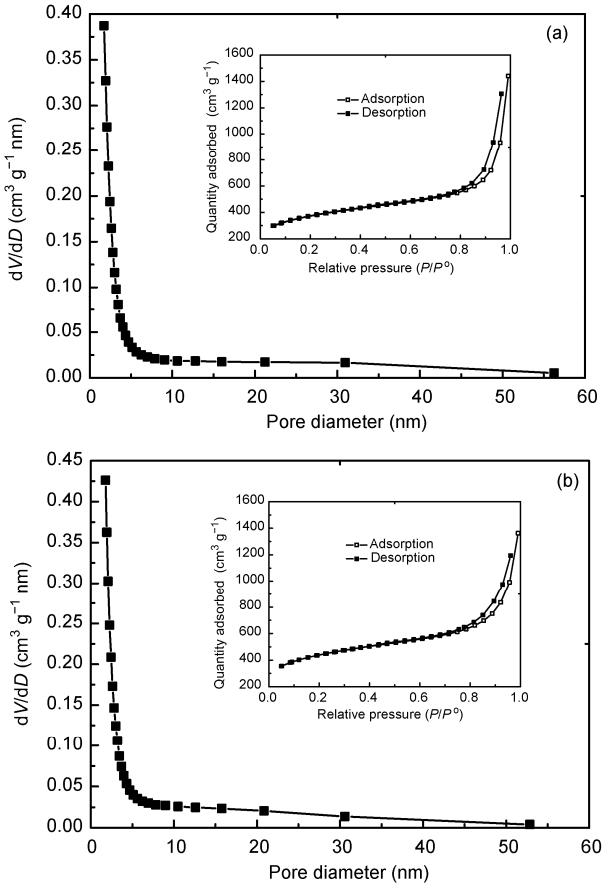

Figure 4 Pore size distribution curves of (a) Co(phen)$_2$/C, (b) BP2000. The inset shows the corresponding N_2 adsorption-desorption isotherm curves.

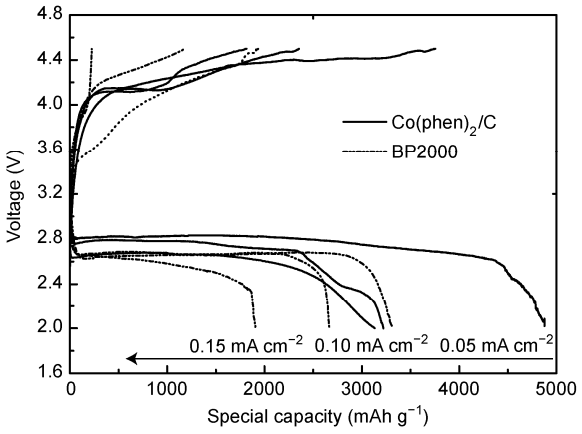

Figure 5 Discharge and charge curves at different current densities corresponding to the first cycle for the Co(phen)$_2$/C cathode and BP2000 cathode.

reversibility of Li_2O_2 (Li_2O) formation and decomposition [1]. Figure 6 compares the cycling performance of the lithium-oxygen cells. The discharge-charge current density was 0.1 mA cm^{-2}. The initial discharge capacity of the $Co(phen)_2$/C cathode was 3274 mAh g^{-1}, which dropped to 2346 mAh g^{-1} at the second cycle and retained a value of 1401 mAh g^{-1} after 10 cycles. The cell with the BP2000 cathode delivered a first discharge capacity of 2667 mAh g^{-1}, which dropped to 620 mAh g^{-1} at the second cycle. The discharge capacity of this cell was only 216 mAh g^{-1} after 10 cycles. The $Co(phen)_2$/C cathode exhibits a favorable discharge and charge cycling performance.

To further understand the electrochemical behavior of the oxygen electrodes, electrochemical impedance spectroscopy was applied and the impedance of the lithium-oxygen cells was measured before the first discharge and after the first charge. Typical Nyquist plots in the frequency range from 0.1 to 10^5 Hz of the cells with $Co(phen)_2$/C and BP2000 cathodes are shown in Figure 7(a) and (b), respectively. All plots exhibit a semicircle in high-to-medium frequency range and a tail in the lower frequency region. The semicircle is mainly related to the charge-transfer kinetic of the oxygen electrode [34,35]. For the $Co(phen)_2$/C cathode, the EIS spectra in Figure 7(a) show that size of the semicircular impedance plot after the first charge is similar to that of the impedance plot recorded before the first discharge. This result means that the charge-transfer reaction ability of the $Co(phen)_2$/C catalyst was well recovered after the first charge. On the contrary, as displayed in Figure 7(b), the EIS spectra of the BP2000 cathode exhibit show that the size of the semicircular impedance plot after the first charge is obviously larger than that of the impedance plot before the first discharge. These may indicate that after the first operation cycle, the BP2000 cathode showed a larger charge-transfer resistance. Comparing Figure 7(a) and (b), it is clear that the cobalt catalyst on the carbon surface improved the charge-transfer reaction kinetics of the oxygen electrode, which in turn, improved the discharge and charge capacities

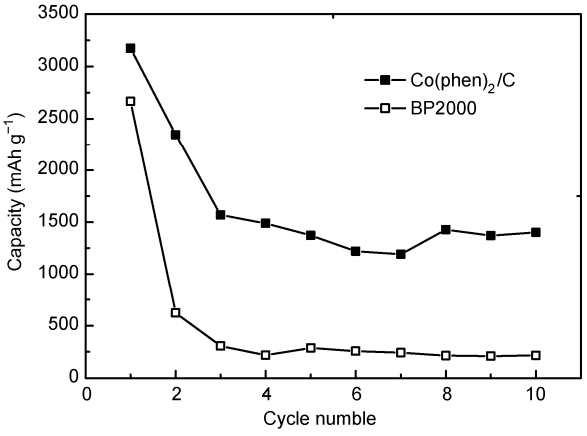

Figure 6 Cycling performance of the lithium-oxygen cells using $Co(phen)_2$/C and BP2000 as catalysts at a discharge-charge rate of 0.1 mA cm^{-2}.

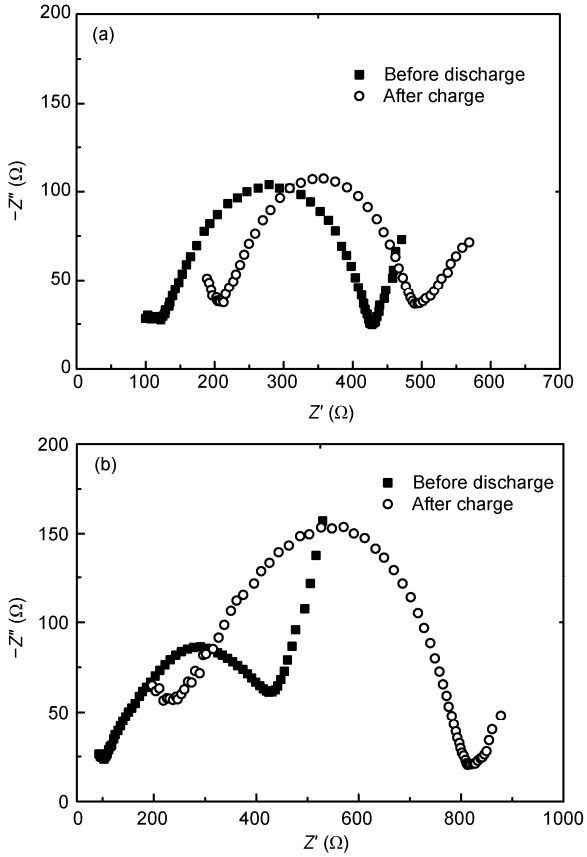

Figure 7 Electrochemical impedance spectra of the lithium-oxygen cells based on (a) the $Co(phen)_2$/C cathode, (b) the BP2000 cathode.

of the lithium-oxygen cell, as shown in Figure 6.

Figure 8 compares the SEM images of $Co(phen)_2$/C cathodes at different stages: (a) before battery assembly, (b) after the first discharge, (c) after the first charge. The discharge and charge current density was 0.1 mA cm^{-2}. It is clear from Figure 8(b) that after 45 h long time discharge (with discharge capacity of 3240 mAh g^{-1}) the discharge product was evenly deposited on the surface of $Co(phen)_2$/C cathode. In the charge process (Figure 8(c)), the as deposited cathode surface was well recovered again.

3 Conclusions

A cheap and active $Co(phen)_2$/C catalyst was successfully prepared and employed in oxygen electrodes for rechargeable lithium air batteries. High discharge capacities of 4870 mAh g^{-1} (0.05 mA cm^{-2}), 3353 mAh g^{-1} (0.1 mA cm^{-2}) and 3220 mAh g^{-1} (0.15 mA cm^{-2}), were obtained under different current densities. This battery also displayed reasonable cycling stability, which means that the cheap $Co(phen)_2$/C catalyst may be a promising candidate for practical application in rechargeable lithium air batteries. Further work on optimizing air electrodes, developing good performance electrolytes and improving battery structure is still ongoing.

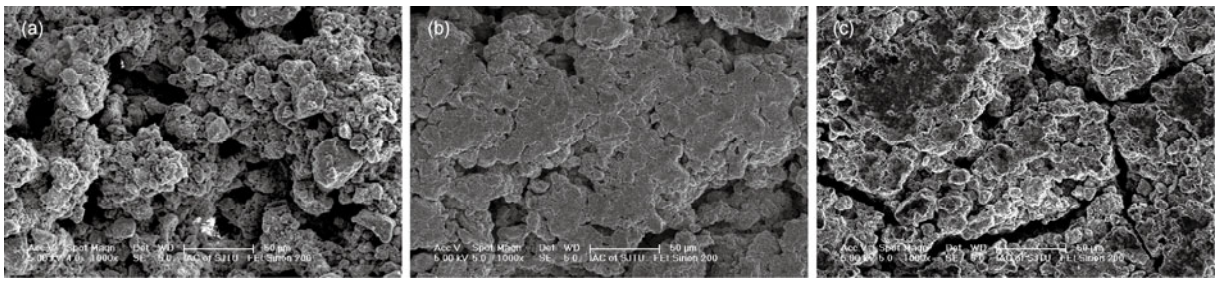

Figure 8 SEM images of oxygen electrodes. (a) Before battery assembly, (b) after the first discharge, (c) after the first charge.

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